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Galilean invariance of the Schrödinger equation in the adiabatic approximation: The central-field method

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In the present work we propose a method for solving the Schrödinger equation in the adiabatic approximation within the molecular context. We employ this method to solve problems with non-Galilean invariance, and an attempt is made to explain some theoretical aspects of it. Simple applications are also considered. This method, which we could call the central-field method (or linear combination of central fields), enables a better understanding of the problem of non-Galilean invariance.

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I. INTRODUCTION

The main aim of this paper is to present an alternative interpretation for the problem of non-Galilean invariance that appears in some semiclassical and quantum adiabatic methods. Some theories specially developed to treat the Coulomb field have operators that are not gauge invariant to the *non-exact* wave functions. In these cases a non-Galilean invariance appears, i.e., some physical quantities will depend on the coordinate origin. These operators are (a) nonadiabatic coupling operators (radial and rotational) [1–3]; (b) dipole operators, which appear in the calculation of oscillator strength in the description of dipole length and dipole velocity gauges [4,5]; (c) multipole operators in the general case, when the preceding multipoles are nonzero. In a molecular or collisional system in the quasimolecule context, the Born-Oppenheimer approximation is usually applied, i.e., the separation of the electronic and nuclear movements. Non-Galilean invariance appears in the nonadiabatic terms introduced by corrections to the adiabatic approximation. This difficulty may be overcome by forcing the method to retain a symmetry of the type found in usual problems of central field, as explained below.

The central-field problem can be described as follows [6]. A two-body problem, whose constituent particles interact by a radial force can be considered as a one-body problem with a reduced mass interacting with the center of mass of the system. Choosing an origin that does not coincide with the central-field origin results in the appearance of noninertial forces, which will make the movement more difficult to describe. Different choices of origin result in different descriptions.

Hydrogenlike atoms are examples of the central-field problems. In general, the nuclear mass is regarded as infinite with respect to the electronic mass. The system center of mass is then located at the nucleus, which is also the most natural inertial frame for the system. The central-field approximation works similarly to the hydrogenlike atom model for atoms of more than a single electron. The situation is more complicated in the case where there is more than one atom (single central field). For simplicity, let us consider a system with two atoms. In the adiabatic approximation described above, where the internuclear distance R is considered as the adiabatic parameter, we define two central fields for each parametric value of R.

If each electron can be regarded as an independent particle, it is possible to reduce the problem of two centers to several problems of one center for each value of the parameter R. This is correct provided the independent particle model is not so restrictive that corrections to the average field (Hartree-Fock) or corrections to the correlation movement must be applied. This point can also be seen as follows. Initially, let us consider that the electron is represented as a probability distribution and that this distribution is written as a linear combination of Gaussian atomic orbitals (particle independent model). Then the general electronic distribution, for the system with two atoms, has two contributions: (a) a contribution of a single atom, where the distribution is centered on a given atom; (b) a contribution of two atoms. The two-atom contribution can be described as a single effective distribution that is generated by both atoms.

Non-Galilean invariance will appear if the origin of the electronic coordinates is *a priori* fixed without agreeing with the several central-field origins. To solve this problem we have developed the central-field method (CFM). In the central-field method each contribution will be solved as a problem of central field. Let $\mathcal{O}$ be any one-electron operator that can be ultimately reduced to a sum of integrals of the type $\langle\varphi_B|\mathcal{O}|\varphi_K\rangle$, e.g., by using the configuration-interaction method or the perturbation theory, where the φ's are the atomic orbitals. These integrals are more generally one-electron integrals of two centers which depend parametrically on the internuclear distance. This two-center problem can be basically transformed into a one-central-field-type description by choosing an origin $\vec{P}_{ij}$,

$$\vec{P}_{ij}=\frac{\alpha_i}{\alpha_i+\alpha_j}\vec{A}+\frac{\alpha_j}{\alpha_i+\alpha_j}\vec{A}', \tag{1}$$

where α_i and α_j are the Gaussian exponents centered on atoms A and A' that are, respectively, localized by the vectors $\vec{A}$ and $\vec{A}'$. This relation is used to transform the product of two Gaussians centered on different centers to a single Gaussian around another intermediate center (see the next section). The new center defined in this way can be seen as having an effective charge that depends both on the electronic distribution and on the nuclei separation. The contrac-

tion of two non-Gaussian distributions is also possible but it would make the system more difficult to treat.

In the CFM all integrals contributing to the operator $\mathcal{O}$ are calculated as a central-field problem. However, it is important to point out that the choice of an origin is made *a posteriori*; that is, the operator is first applied to the Gaussian basis and then the integral is carried out analytically by choosing the central-field origin defined by Eq. (1). The determination of the operators by this method makes some problems that arise in the limit of separated atoms easier to solve and understand. For a fixed origin, if both functions are centered on the same atom (contribution of a single atom), the parametric dependence with R still exists; the only exception is $R=0$.

The main interest of this paper is to justify the description of collisions in the semiclassical approximation at intermediate collisional kinetic energies [7,8] without making reference to any *ad hoc* function such as the translation factor [1,9–13].

II. THEORY AND METHOD

Our starting point is the time-dependent Schrödinger equation

$$i\partial\Xi(\vec{r},\vec{R},t)/\partial t = H\Xi(\vec{r},\vec{R},t), \tag{2}$$

where $\Xi(\vec{r},\vec{R},t)$ is the wave function, $\vec{r}$ and $\vec{R}$ are, respectively, the electronic and nuclear coordinates. We will show that the Galilean invariance is also valid in the Schrödinger equation in the adiabatic approximation.

By separating the electronic and nuclear motions in Eq. (2) we have

$$i\partial\Psi(\vec{r},t;\vec{R})\chi(t,\vec{R})/\partial t = -1/(2\mu)\nabla_R^2|_{\vec{r}}\Psi(\vec{r},t;\vec{R})\chi(t,\vec{R}) + H_{\rm el}(\vec{r},\vec{R})\Psi(\vec{r},t;\vec{R})\chi(t,\vec{R}), \tag{3}$$

where Ψ and χ are, respectively, the electronic and nuclear wave functions. $H_{\rm el}$ is the electronic Hamiltonian and, for simplicity, a diatomic system is considered. Some unimportant terms were neglected in Eq. (3) [11]. We assume that the nuclei are moving along classical paths $R(\vec{v},\vec{b},t)$ (semiclassical approximation), where v is the classical nuclear velocity and b is the impact parameter. In this approximation, Eq. (3) can be written as

$$i\partial\Psi(\vec{r};\vec{R}(t))/\partial t = H_{\rm el}(\vec{r};\vec{R}(t))\Psi(\vec{r};\vec{R}(t)), \tag{4}$$

since the nuclear wave function can be represented by a plane wave. t is now the classical time.

The total wave function Ψ of Eq. (4) in the perturbative stationary state approximation is given by [11]

$$\Psi(\vec{r},t;\vec{R}) \approx \sum_{n=1}^{N} a_n(t)\Psi_n(\vec{r};\vec{R})f_n(t), \tag{5}$$

where $\Psi_n(\vec{r};\vec{R})$ is the orthonormal Born-Oppenheimer electronic wave function that satisfies the relation $H_{\rm el}\Psi_n=\epsilon_n\Psi_n$. The function $f_n(t)=\exp[-i\int_{-\infty}^{t}\epsilon_n(R(t'))dt']$ is related to the dynamical phase, and N is the (finite) total number of states.

It is known that Eq. (2) is Galilean invariant and it would be useful if Eq. (4) had the same property. In order to make Eq. (4) also Galilean invariant, we apply our CFM. If the approximation Eq. (5) is substituted in Eq. (4), and the resulting terms are multiplied by $\Psi_m f_m(t)$ and followed by an integration, we find

$$a_m(t)\epsilon_m \approx \sum_{n=1}^{N} \langle \Psi_m f_m(t)|i\partial/\partial t|a_n(t)\Psi_n f_n(t)\rangle, \tag{6}$$

where ϵ_m is the electronic energy eigenvalue. Ψ_l can be represented by a linear combination of atomic orbitals [14], so that Eq. (6) becomes

$$a_m(t)\epsilon_m \approx \sum_{n=1}^{N}\sum_{i,j} \langle f_m b_i^m\varphi_i|i\partial/\partial t|a_n f_n b_j^n\varphi_j\rangle, \tag{7}$$

where $\{\varphi_k\}$ is the atomic basis and $\{b_k\}$ are contractions of several coefficients for each value of the adiabatic parameter R [7]. This contraction involves the atomic components of the molecular orbitals and coefficients of the configuration-interaction expansion that are computed by a variational method. It also includes the fixed coefficients of the determinants defining each configuration-state function. This reduction from configuration-state function to atomic functions is suitable since the operator for the nonadiabatic coupling will obey the rules of a one-electron operator.

The problem with non-Galilean invariance arises because different approximations are used for different terms in Eq. (7). The electronic Hamiltonian $H_{\rm el}$ has one- and two-electron operators. An explicit expansion in terms of atomic orbitals is more difficult to be obtained for the two-electron operators. Nevertheless, since the electronic Hamiltonian that is represented by the electronic energy ϵ_m depends only on internal coordinates of the whole system, the left-hand side of Eq. (7) does not depend on the origin of integration. This origin can then be fixed anywhere and, in particular, it can be fixed at the central-field center; that is, the left-hand side of Eq. (7) is a Galilean-invariant term. It can be generally shown that if $H_{\rm el}$ depends only on internal coordinates, it also does not depend on the origin of integration. A component of the vector operator of the kind $\partial/\partial x_i^{(\alpha A)}$ or $x_i^{(\alpha A)}$ in $H_{\rm el}$, for example, $x_i^{(\alpha A)}$ can be written in Cartesian coordinates by

$$x_i^{(\alpha A)} = x_i^{(\alpha)} - x_i^{(A)},$$

where $x_i^{(\alpha A)}$ is the ith component of the position vector of the electron α relative to the nucleus A, $x_i^{(\alpha)}$ and $x_i^{(A)}$ are, respectively, the ith components of the position vector for the electron α and the nucleus A. These vectors are fixed relative to an origin O. If we exchange the origin O with O', it results in

$$x_i^{(\alpha')} = x_i^{(\alpha)} - x_i^{(O')}$$

and

$$x_i^{(A')} = x_i^{(A)} - x_i^{(O')},$$

where $x_i^{(O')}$ is the ith component of the displacement vector. The vector $x_i^{(\alpha A)}$ $(=x_i^{(\alpha)}-x_i^{(A)}=x_i^{(\alpha')}-x_i^{(A')})$ becomes invariant for any origin. The same is also valid for operator $\partial/\partial x_i^{(\alpha A)}$. The z component of this operator is explicitly given in Eqs. (20), (21), and (27) with $f_{\rm rad}=f_{\rm rad}^1=1$ and, therefore, it does not depend on the origin of integration. In this way we conclude that both the right-hand side of Eq. (7) and all terms in Eq. (4) must be Galilean invariant in order to preserve this symmetry of the whole system described by Eq. (4) or Eq. (7). In addition, a solution for any operator of a linear equation expressed as a linear combination of *bra-ket* integrals is Galilean invariant only if each integral term is Galilean invariant, so that each term must be calculated by the CFM in order to preserve this symmetry.

The integrals

$$\langle\varphi_i|i\partial/\partial t|\varphi_j\rangle, \tag{8}$$

that appear in Eq. (7) depend on the origin of the electronic coordinates according to some usual approaches [15]. These integrals must be solved by the CFM to maintain the Galilean invariance; see the overlap calculation and the following. Therefore, Eq. (8) can be written as $\langle\varphi_i|i\partial/\partial t|_{r_{ij}}|\varphi_j\rangle$, where r_{ij} is the origin of integration in the internuclear axis that is suitably chosen to obey the CFM. The recipe for this method is to apply the procedure of the central field to any operators without any other modification in the usual theory.

A system of coupled equations for any origin of the electronic coordinates is obtained [1] from Eq. (4) together with the general solution Eq. (5),

$$i\,\frac{da_m(t)}{dt}=\sum_{n=1}^{N} M_{mn}a_n(t)\exp\left(-i\int_{-\infty}^{t}(\epsilon_n-\epsilon_m)dt'\right), \tag{9}$$

where $M_{mn}(t)$ is the coupling term that is given in the CFM case by

$$M_{mn}(t)=\langle\Psi_m|H_{\rm el}-i\partial/\partial t|_{\vec{r}_{ij}}|\Psi_n\rangle. \tag{10}$$

Here $\vec{r}_{ij}$ refers to a suitable origin for each (ij) pair of atomic orbital functions.

The relation between the operator $i\partial/\partial t$ in the laboratory frame L and in the molecular frame M is expressed by

$$i\partial/\partial t|_L=i(v^2t/R)\partial/\partial R|_M+i(vb/R^2)\sum_{j=1}^{n} iL_y(j)|_M, \tag{11}$$

where the operator $iL_y(j)=(z\partial/\partial x-x\partial/\partial z)$ is the y component of the angular momentum for the electron j; $\partial/\partial R$ and iL_y are, respectively, the radial and rotational (Coriolis) couplings.

If Ψ_n is a configuration-interaction (CI) wave function the coupling terms are determined by

$$\langle\Psi_m|\partial/\partial R|\Psi_n\rangle=\sum_i C_i^m\partial C_i^n/\partial R+\sum_{\alpha\beta}P_{\alpha\beta}^{mn}\left(\sum_{p\neq q}a_p^\alpha[a_q^\beta\langle\varphi_p|\partial/\partial R|\varphi_q\rangle+\langle\varphi_p|\varphi_q\rangle\partial a_q^\beta/\partial R]+\sum_p a_p^\alpha\partial a_p^\beta/\partial R\right) \tag{12}$$

and

$$\langle\Psi_m|iL_y|\Psi_n\rangle=\sum_{\alpha\beta}P_{\alpha\beta}^{mn}\sum_{pq}a_p^\alpha a_q^\beta\langle\varphi_p|iL_y|\varphi_q\rangle, \tag{13}$$

where C_i^n are the CI coefficients, $P_{\alpha\beta}^{mn}$ represent the element $\alpha\beta$ of the transition density matrix between the Born-Oppenheimer states Ψ_m and Ψ_n in the molecular base $\{\alpha,\beta\}$, and a_p^α are the self-consistent-field results coefficients.

In Eqs. (12) and (13) the terms

$$\langle\varphi_p|\partial/\partial R|\varphi_q\rangle \tag{14a}$$

and

$$\langle\varphi_p|iL_y|\varphi_q\rangle, \tag{14b}$$

are noninvariant since they depend on the origin [15]. These integrals can be calculated in any fixed electronic coordinate origin or in the origin of the central-field problem (r_{pq}), as explained in the Introduction. We present below an explicit calculation of these integrals.

Many standard numerical calculations of the atomic orbitals are carried out with a linear combination of Gaussian functions,

$$\varphi_p=\sum_{\mu=1}^{C_p} d_{\mu p}N_{nlm}(\alpha)\Phi_{\mu p}(n,l,m,\alpha_A,A), \tag{15}$$

where $\Phi_{\mu p}(n,l,m,\alpha_A,A)=x_A^n y_A^l z_A^m\exp(-\alpha_A r_A^2)$ are Cartesian Gaussian functions, $d_{\mu p}$ are expansion coefficients,

$$N_{nlm}=(2\alpha_A/\pi)^{3/4}[(4\alpha_A)^{n+l+m}/(2n-1)!!\times(2l-1)!!(2m-1)!!]^{1/2}\quad(n,l,m\geqslant 0)$$

are the Gaussian normalization constants, $\vec{r}_A=\vec{r}-\vec{A}$, and $\vec{A}$ is the position of the atom A. Using such Gaussian functions it is not difficult to separate the three-dimensional (3D) integral $(\langle\varphi_p|\partial/\partial t|\varphi_q\rangle)$ into three independent one-dimensional integrals. As an example we solve the overlap integral for a fixed origin according to the CFM. The basic overlap integral is $\Omega=\langle\Phi_{\mu p}(n,l,m,\alpha_A,A)|\Phi_{\nu p}(n',l',m',\alpha_{A'},A')\rangle$. For a system of two atoms with the internuclear vector (R) along the z axis we have the following three-dimensional (3D) equation:

$$\Omega=\langle x^{n+n'}y^{l+l'}z_A^m z_{A'}^{m'}\exp[-(\alpha_A r_A^2+\alpha_{A'}r_{A'}^2)]\rangle, \tag{16}$$

where the exponential factor can be written as [16] $\exp[-(\alpha_A\alpha_{A'}/\alpha)|\vec{A}'-\vec{A}|^2]\exp(-\alpha r_P^2)$, with $|\vec{A}'-\vec{A}|=R$, $\vec{r}_P=\vec{r}-P$, $\vec{r}$ is the position of the electron, $\alpha=\alpha_A+\alpha_{A'}$, and

$\vec{P}=(\alpha_A\vec{A}+\alpha_{A'}\vec{A}')/\alpha$. The integration in Eq. (16) runs over the 3D electronic coordinates since Ω is a one-electron integral; the subindices denote only the relative origin for the electronic variable. The $\Omega_{(k)}$ integral, Eq. (16) is just one of the terms of the product that define the total overlap integral ($\Omega_{\text{total}}=\Omega_1\Omega_2\cdots\Omega_n$) for n electrons, since we have considered the independent particle model. Equation (16) can be rewritten [16] as

$$\Omega=\exp\left(-\frac{(\alpha_A\alpha_{A'})}{\alpha}R^2\right)\langle x^{n+n'}\exp(-\alpha x^2)\rangle \times\langle y^{l+l'}\exp(-\alpha y^2)\rangle\langle(z-A)^m(z-A')^{m'} \times\exp[-\alpha(z-P)^2]\rangle, \tag{17}$$

which is also a 3D integral.

For the origin in the center of mass (CM) we have for Eq. (17) $A=[m_{A'}/(m_A+m_{A'})]\vec{R}$, $A'=-[m_A/(m_A+m_{A'})]R$, and since $\vec{P}=(\alpha_A\vec{A}+\alpha_{A'}\vec{A}')/\alpha$, then $\vec{P}=[(\alpha_Am_{A'}-\alpha_{A'}m_A)/(m_A+m_{A'})\alpha]\vec{R}$. For the origin in the geometric center (GC) $A=-A'=R/2$ and $\vec{P}=[(\alpha_A-\alpha_{A'})/2\alpha]\vec{R}$. Now, we define the origin of the CFM by $A=\alpha_{A'}R/\alpha$, $A'=-\alpha_AR/\alpha$ and $\vec{P}=\vec{0}$. Of course the Ω integral presents the same result for any origin of integration and it is

$$\Omega=\exp\left[-\frac{(\alpha_A\alpha_{A'})}{\alpha}R^2\right]I_x^{n,n'}I_y^{l,l'}I_z^{m,m'}, \tag{18}$$

where $I_w^{k,k'}$ represents the corresponding integral that appears in Eq. (17). The overlap integral is

$$\Omega=\exp\left[-\frac{(\alpha_A\alpha_{A'})}{\alpha}R^2\right]G(N+1)G(L+1)\sum_{i=0}^{m}\sum_{j=0}^{m'}(-1)^j\binom{m}{i}\binom{m'}{j}\alpha^{-(N+L+M-i-j+3)/2}\left(\frac{\alpha_{A'}R}{\alpha}\right)^i\left(\frac{\alpha_AR}{\alpha}\right)^jG(M-i-j+1), \tag{19}$$

where

$$G(\xi)=\begin{cases}0 & \text{if } \xi=\text{even integer}\\ \Gamma(\xi/2)=[1\times3\times\cdots\times(\xi-2)]\pi^{1/2}2^{-(\xi-1)/2} & \text{if } \xi=\text{odd integer,}\end{cases}$$

$N=n+n'$, $L=l+l'$, $M=m+m'$, and $\binom{n}{k}$ is the binomial coefficient. The overlap integral goes as $\exp(-R^2)$ as a consequence of the Gaussian basis functions. The correct dependence is obtained by using a linear combination of Gaussian functions [8].

For the integrals of the nonadiabatic radial coupling we have

$$\langle\Phi_B(n_B,l_B,m_B,\alpha_B,\vec{A}_B)|\partial/\partial R|\Phi_K(n_K,l_K,m_K,\alpha_K,\vec{A}_K)\rangle=\exp\left[-\frac{\alpha_B\alpha_K}{\alpha}R^2\right]I_x^{n_B,n_K}I_y^{l_B,l_K}A_K(2\alpha_KI_z^{m_B,m_K+1}-m_KI_z^{m_B,m_K-1}), \tag{20}$$

where A_K is defined for each origin of integration (see calculation of the overlap). Note that the presence of the term A_K in Eq. (20) implies non-Galilean invariance. Only for one particular value of A_K the equation is Galilean invariant (see Sec. III). Here the subindices of the Φ functions and their exponents were changed to (B,K), where B and K label, respectively, the functions in the *bra* and *ket* vectors.

Finally we have for the radial coupling [7,8]

$$\langle\Phi_B|\partial/\partial R|\Phi_K\rangle=\exp\left[-\frac{\alpha_B\alpha_K}{\alpha}R^2\right]G(N+1)G(L+1)\sum_{b=0}^{m_B}\sum_{k=0}^{m_K+1}(\hat{\vec{A}}_B\cdot\hat{\vec{R}})^b(\hat{\vec{A}}_K\cdot\hat{\vec{R}})^{k+1}\binom{m_B}{b}\binom{m_K+1}{k}\left(\frac{\alpha_KR}{\alpha}\right)^b\left(\frac{\alpha_BR}{\alpha}\right)^k \times G(M-b-k)\alpha^{-(N+L+M-b-k+2)/2}(f_{\text{rad}})\left(\frac{(m_K+1-k)(m_K-k)}{m_K+1}-\frac{\alpha_K(M-b-k)}{\alpha}\right), \tag{21}$$

for the two-center integral, i.e., each function is centered on a distinct atom. For the one-center integral we have

$$\langle\Phi_B|\partial/\partial R|\Phi_K\rangle=G(N+1)G(L+1)G(M)(\hat{\vec{A}}_K\cdot\hat{\vec{R}})\alpha^{-(N+L+M+2)/2}(f^1_{\text{rad}})(m_K-\alpha_KM/\alpha). \tag{22}$$

And for the rotational coupling [7,8]

$$\langle\Phi_B|iL_y|\Phi_K\rangle=\exp\left[-\frac{\alpha_B\alpha_K}{\alpha}R^2\right]G(N)G(L+1)\sum_{b=0}^{m_B}\sum_{k=0}^{m_K+1}(\hat{\vec{A}}_B\cdot\hat{\vec{R}})^b(\hat{\vec{A}}_K\cdot\hat{\vec{R}})^k\binom{m_B}{b}\binom{m_K+1}{k} \times\left(\frac{\alpha_KR}{\alpha}\right)^b\left(\frac{\alpha_BR}{\alpha}\right)^k\frac{\alpha^{-(N+L+M-b-k+3)/2}}{2(m_K+1)}\{G(M-b-k)[N(m_K+1-k)(m_K-k)-(M-b-k)kN\alpha_K/\alpha -n_K(M-b-k)(m_K+1-k)]+(2R/\alpha^{1/2})G(M-b-k+1)(f_{\text{rot}})(m_K+1-k)(\alpha_KN-\alpha n_K)\}, \tag{23}$$

for the two-center integral. For the one-center integral the last relation can also be written as

$$\langle\Phi_B|iL_y|\Phi_K\rangle = G(N)G(L+1)(\hat{\vec{A}}_K\cdot\hat{\vec{R}})\alpha^{-(N+L+M+4)/2}[G(M)(\alpha^{1/2}/2)(Nm_K - Mn_K) + G(M+1)R(f^1_{\rm rot})(\alpha_K N - \alpha n_K)]. \tag{24}$$

Here $\hat{\vec{A}}_B$ and $\hat{\vec{A}}_K$ are unity vectors of the position atomic vectors whose Gaussian functions are, respectively, located in the *bra* or *ket*. $\hat{\vec{R}}$ is a unity vector in the internuclear axis. The inner vector product $(\hat{\vec{A}}\cdot\hat{\vec{R}})$ possess only two values (± 1). The values for $f_{\rm rad}$ and $f^1_{\rm rad}$ in Eqs. (21) and (22) $f_{\rm rot}$ and $f^1_{\rm rot}$ in Eqs. (23) and (24) according to the origin are found below.

	CFM	GC	CM
$f_{\rm rad}$	α_B/α	1/2	M_B/M
$f^1_{\rm rad}$	0	1/2	M_B/M
$f_{\rm rot}$	0	$(\alpha_K-\alpha_B)/2\alpha$	$(\alpha_K M_B-\alpha_B M_K)/M\alpha$
$f^1_{\rm rot}$	0	1/2	M_B/M

where M is the total mass $(M=M_B+M_K)$.

III. RESULTS

The dynamical couplings are the most important applications of the CFM in this paper. Some results can be found in Refs. [7] and [8]. A simple analysis of Eqs. (22)–(24) can be performed to verify the asymptotic behavior $R\to\infty$. For intermediate values of R the analysis is more difficult. Equations (21) and (23) involving two-center integrals with the factor $\exp[-[(\alpha_B\alpha_K)/\alpha]R^2]$ go to zero in the limit $R\to\infty$, which means that the analysis can be restricted to the one-center integral only. Equation (22) in the CFM is zero since the origin of integration is localized in the atom and it does not depend on the parameter R. For other fixed origins Eq. (22) is equal to

$$\langle\Phi_B|\partial/\partial R|\Phi_K\rangle = \delta\langle\Phi_B|\partial/\partial z|\Phi_K\rangle, \tag{25}$$

for the radial coupling, where δ is the distance of the origin fixed at the atom $(R\delta)$ divided by R and the integral is the linear transition momentum $[\langle\Psi_1|\partial/\partial z|\Psi_2\rangle = (E_2-E_1)\langle\Psi_1|z|\Psi_2\rangle$ for the exact wave function].

In the case of coupled states with the same parity (g or u) where in the $D_{\infty h}$ group the linear momentum operator has a u symmetry and the transition momentum is zero, the calculation of the radial coupling for a homonuclear system is the same no matter the choice of origin. However, if the radial coupling integral involves u and g states, this integral will be constant (non-null by symmetry) in the limit $R\to\infty$ for any fixed origin.

A more complete discussion follows from Eq. (11),

$$\langle\Psi_1|\partial/\partial R|\Psi_2\rangle|_O = \langle\Psi_1|\partial/\partial R|\Psi_2\rangle|_{O'} + \delta\langle\Psi_1|\partial/\partial z|\Psi_2\rangle, \tag{26}$$

where O and O' are two fixed origins of the electronic coordinates and δ is the distance between O and O' divided by R.

In the limit $R\to\infty$ the central-field "center" can be considered as a "good vector," i.e., it can be trivially located, e.g., by O'. The integral in O' is zero, since the one-center integral does not depend on R. But Eq. (22) is nonzero for N and L even and M odd for any fixed origin, i.e., when the linear transition momentum $(\partial/\partial z)$ is also nonzero. Equation (22) can be written in the form

$$\langle\Phi_B|\partial/\partial R|\Phi_K\rangle = (f^1_{\rm rad})\langle\Phi_B|\partial/\partial z|\Phi_K\rangle, \tag{27}$$

and similarly Eq. (21).

The nonzero value of the one-center radial coupling integral in the limit $R\to\infty$ is physically incorrect. It implies the possibility of self-transitions caused exclusively by a linear atomic motion. This is clearly a non-Galilean-invariant result [2] and is normally corrected with the translation factor [9]. In spite of the similarity of the numerical results of the translation factor to those of the CFM, the use of the CFM is simpler and presents a clearer physical interpretation than the procedures of the translation factor. The same kind of analysis can be made to the rotational coupling. Equation (24) has two components; the first is the angular momentum of the central field and the second is a component due to the fact that the origin of the coordinates does not agree with the origin of the angular motion.

Equation (26) or (27) for the rotational coupling is

$$\langle\Phi_B|iL_y|\Phi_K\rangle = \mathscr{M}_{\rm CFM} + (f^1_{\rm rot})R\langle\Phi_B|\partial/\partial x|\Phi_K\rangle, \tag{28}$$

where the $\mathscr{M}_{\rm CFM}$ term is the angular momentum of the CFM that has $f^1_{\rm rot}=0$ and $\partial/\partial x$ is the x component of the linear momentum; $f^1_{\rm rot}$ is not zero for other origins. The first term on the right-hand side of Eq. (24) is nonzero for N and M odd and L even. It exists for any origin and it is an invariant term. This integral is exact, for example, $\langle\Psi_{2px}|iL_y|\Psi_{2pz}\rangle=1$ (considering the normalization constant), provided $N=M=1$, $L=0$, and Ψ_{2px} and Ψ_{2pz} have arbitrarily the same exponent. $\Psi_{2px}(n=1,\ m=l=0)$ and $\Psi_{2pz}(n=l=0,\ m=1)$ are defined for the n, m, and l parameters in Eq. (15) with $C_p=1$. The second term of Eq. (24) is nonzero for N odd and L and M even. This term is proportional to R, and for this case, the first term is zero and the rotational coupling (iL_y) increases with R.

The former analyses can be simplified by the Wigner-Eckart theorem. We can show that if the radial coupling $(\partial/\partial R)$ depends on the origin, then the rotational coupling (iL_y) for the correspondent states will be dependent on the origin, too.

For the CFM, or a linear combination of the central fields the radial $(\partial/\partial R)$ and rotational (iL_y) couplings decay, respectively, as R^{-3} and R^{-2} for very large internuclear distances [8,17] when the Stark effect is also present. In this case for any fixed origin the radial coupling $(\partial/\partial R)$ is constant and the rotational coupling (iL_y) increases with R. Therefore this result also eliminates the physically unacceptable transition at infinity and it also avoids the use of an *ad hoc* translation factor. Many methods were proposed to correct the problems of non-Galilean invariance. One of the

most recent is the dynamical adiabatic approach [18,19]. This approach is more complex than the CFM.

The solution using the CFM is sufficiently accurate so that translation factor corrections are small [7,8]. The simplest of all seems to be the CFM, in comparison with other methods in the molecular approximation.

Problems with origin dependence also occur in other systems. For example, they can occur in the choice of gauge for the calculation of the oscillator strength. Examples are the electric-field gauge in the dipole approximation and the radiation gauge [4,5]. From a theoretical point of view the electric-field and radiation gauges are both equivalent, but for nonexact wave functions this is not true [4]. Nevertheless for approximate wave functions these gauges are similar according to the CFM. See Ref. [4] as an example.

The oscillator strength f is expressed in atomic units (a.u.) ($\hbar=1$, $m=1$) by

$$f=(4\pi/3)\nu|Q|^2 \tag{29}$$

with

$$|Q|=|\langle\Psi_B|z|\Psi_K\rangle|, \tag{30}$$

in the electric-field gauge approximation or by

$$|Q|=(2\pi\nu)^{-1}\langle\Psi_B|\partial/\partial z|\Psi_K\rangle, \tag{31}$$

in the radiation gauge approximation, where ν is the radiation frequency ($\nu=\Delta E/2\pi$), and ΔE is the energy difference of the states.

If Ψ is a linear combination of atomic orbitals (LCAO) that describe the H_2^+ system [4] then $\Psi_{(1s)\sigma_g}=[2(1+S)]^{-1/2}[\Phi_{1s}(A)+\Phi_{1s}(A')]$ and $\Psi_{(2p)\sigma_u}=[2(1-S)]^{-1/2}[\Phi_{1s}(A)-\Phi_{1s}(A')]$, where S is the overlap integral, $\Psi_{(1s)\sigma_g}$ is the ground state of the H_2^+ and $\Psi_{(2p)\sigma_u}$ is the first excited state. The Φ_{1s} is the hydrogenic wave function for the ground state. In the following discussion, instead of considering directly hydrogenic orbitals, it will be enough to only consider the corresponding Gaussian functions. The integral appearing in Eq. (31) is zero for the $\Psi_{(1s)\sigma_g}$ and $\Psi_{(2p)\sigma_u}$ wave functions in the limit $R\to\infty$ [4]. The corresponding two-center integrals decrease exponentially as a function of R and the one-center integrals are zero by symmetry in the limit $R\to\infty$. The linear momentum transition is given by Eqs. (27) and (22), and it is nonzero for N and L even and M odd. Since the wave function $\Psi_{(1s)\sigma_g}$ and $\Psi_{(2p)\sigma_u}$ have $N=L=M=0$ the linear momentum transition is zero if $R\to\infty$.

However, Eq. (30) has a nonzero value for any fixed origin in the limit $R\to\infty$ [4] [except for the particular case with a fixed origin in the H atom, since in this case it coincides with the CFM results. If Eq. (30) had other states (or systems) its value could be different].

The normalized one-center dipole integral for the origin of the geometric center (or center of mass) in the limit $R\to\infty$ is easily calculated and is given by

$$\langle\Psi_B|z|\Psi_K\rangle|_{\text{GC or CM}}=\langle\Psi_B|z|\Psi_K\rangle|_{\text{CF}}+R/2\langle\Psi_B|\Psi_K\rangle, \tag{32}$$

where the CF (''origin'' of the CFM) dipole integral has the same symmetry as the $(\partial/\partial z)$ integral. The last term is the monopole contribution and, in the considered limit, the one-center integral $\langle\Phi_{1s}|\Phi_{1s}\rangle$ is unitary.

The asymptotic Bates' result of the (LCAO) dipole length is $R/2$ [4]. This result was obtained considering the origin of the center of mass (or geometric center). We have similar invariant results for the two gauges in the CFM; however, in this work we only discuss asymptotic limits. In the CFM the monopole term does not contribute to the invariant result.

For any kind of basis functions, Gaussian functions or others, the one-center radial coupling integral is zero for the CFM, as this integral does not depend on R. Otherwise, for any fixed origin, it is not always zero. According to the CFM the values of the rotational coupling are the angular momentum given in Eq. (28). Another component will appear that depends on the origin choice if any other origin is chosen.

The CFM can also be used to calculate the radial coupling by the Hellmann-Feynman theorem or by the Sidis' formula [20]. The problem of non-Galilean invariance for nonexact wave function is drastically minimized by this method as in the case of the determination of the oscillator strength.

For diatomic systems (internuclear vector R coinciding with the z axis) the components of the multipole expansion are given by

$$\langle x^i y^j z^k\rangle|_O=\sum_{s=0}^{k}(-1)^s\binom{k}{s}[f_O(\delta R)]^s\langle x^i y^j z^{k-s}\rangle|_{\text{CF}}, \tag{33}$$

where $\langle x^i y^j z^k\rangle$ is the component of the $(i+j+k)$th multipole tensor, O and CF are, respectively, any fixed origin and the ''origin'' of the CFM. $f_O(\delta R)$ are functions depending on δR and the origin O, and δR is defined in Eq. (25). For intermediate values of R, the vector δR is not a ''good vector'' if the center-field origin is taken as reference. The multipole tensors calculated by the CFM ($\langle x^i y^j z^k\rangle|_{\text{CF}}$) are invariant.

Our method can be applied in semiclassical approaches, as in the case of the translation factor or in adiabatic quantum methods, which constitutes another advantage. In the adiabatic quantum calculation a correction to the non-Galilean invariance is also difficult and complex, since either we have to calculate the quantum version of the translation factor or use the reaction coordinates [3,21]. However, in CFM there is no need for correcting explicitly the non-Galilean invariance problem. The matrix elements determined by the CFM are also Galilean invariant. It is possible to apply the CFM for studying systems with more than two atoms. The integrals are calculated for each atom pair as a diatomic problem. The central-field origin is always defined for each function pair, and such a procedure is as simple as the case of diatomic systems.

IV. CONCLUSION

The main result of this paper is to show that the non-Galilean invariance problem [2] can be understood as a central-field problem. In order to solve the non-Galilean invariance problem applications to some systems were made. The CFM can provide results only for Gaussian basis functions. Application of the CFM to physical wave functions

requires a linear combination of basis functions, whose coefficients can be found by a variational, or similar technique [7,8]. The generalization of the integral calculation for a non-Gaussian distribution can be done, but perhaps only numerically. One advantage of the CFM is the preservation of Galilean invariance in the many integrals that a molecular-orbital calculation requires.

The CFM can be viewed as a zero-order correction in a practical way, i.e., it is not necessary to emphasize the Galilean invariance problem, e.g., in scattering problem it is not required to emphasize the translation factor or other *ad hoc* factor. This method can be applied to both semiclassical and quantum theory. The CFM can provide good results, even when nonexact wave functions are used, a procedure in which other methods will probably fail. For the multipole expansion the invariant terms can also be determined. This procedure is an option relatively to other methods such as the translation factor [8].

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